Stability of Chemically Modified Indium–Tin–Oxide Surfaces against Water

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We studied stability of indium–tin–oxide (ITO) surfaces chemically modified with $-SO_2Cl$ and $-PO_2Cl_2$ binding groups of para substituted benzene derivatives as well as those oxidized with UV ozone by measuring time dependence of the work function and water contact angle after their surface modifications. It seems most likely from the effect of water contents in environments upon their time changes that water is the primary reactant for degradation of the chemically modified and oxidized ITO surfaces.

Organic light-emitting diodes (OLEDs),[1] organic photovoltaics,[2] and dye-sensitized solar cells[3] have attracted attention owing to their ease of fabrication, potential for low-cost production, and compatibility with flexible substrates.[4] As optically transparent electrode materials for these optoelectronic devices, indium–tin–oxide (ITO) or SnO_2 has been used widely.[5] However, for enhanced hole injection and open-circuit voltages, matching between the Fermi level of the oxide electrode and the highest occupied molecular orbital level of the organic layer is required.[4–6] Therefore, changing the work function (ϕ) of these oxide electrodes has been attempted by surface treatment with adsorption of acids and bases,[7] self-assembled monolayer (SAM) formation with polar adsorbate molecules,[8] and exposure to O_2 plasma[9] or UV ozone.[10] Among them, we have demonstrated tuning ϕ by chemical modification of ITO surfaces with various acid chloride (i.e., $-SO_2Cl$, $-COCl$, and $-PO_2Cl_2$) binding groups of para-substituted benzene derivatives.[8c] Similar chemical modification methods were used for the first time by us for enhanced dye sensitization current on SnO_2.[5,11]

However, acid treatment was not reliable and an abrupt decrease of ϕ was observed.[7c] So far, silanized surfaces are considered to exhibit improved durability because of their adherence to the oxide surfaces via covalent bonds.[4a,8b] To the best of our knowledge, none have studied stability of the chemically modified surfaces with acid chlorides in detail.[5]

In this work, the degradation processes of the chemically modified as well as oxidized ITO surfaces with UV ozone (ITO(uv)) were studied by measuring the time change in ϕ or water contact angle (CA) after exposure of freshly prepared samples to various environments. In particular, we focused our attention on the effect of water in the environments.

Three kinds of modified ITO electrodes (i.e., Cl-S, CF_3-S, and Cl-P in Figure 1) as well as ITO(uv) ($12 \times 15\,mm^2$)[12] were prepared as previously.[8c] Values of ϕ were measured more carefully than in the previous study,[8c] because tip and time dependence of observed ϕ values were not negligible.[13]

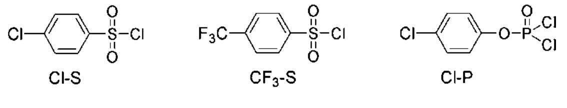
Cl-S CF$_3$-S Cl-P

Figure 1. Chemical structures of modifiers and abbreviations for the resulting chemically modified ITO surfaces.

Table 1. Averaged initial ϕ and CA values observed on the three kinds of modified and oxidized samples

Sample	Initial		After dipping in pure water	
	ϕ/eV	CA/°	ϕ/eV	CA/°
CF_3-S	5.50 ± 0.09	37 ± 5	4.64 ± 0.05	11 ± 2
Cl-S	5.06 ± 0.10	37 ± 8	4.66 ± 0.06	12 ± 3
Cl-P	5.09 ± 0.10	56 ± 6	4.70 ± 0.04	14 ± 4
ITO(uv)	5.01 ± 0.12	11 ± 3	4.67 ± 0.08	11 ± 3

Averaged initial ϕ and CA values[13] observed on the three kinds of modified and oxidized samples over the number (n) of each sample ($n > 10$) are listed in Table 1. In Figure 2a are shown the time change in ϕ after exposure of the samples to environments with two different relative humidities (RHs) at room temperature. Because the large shifts in ϕ from those of cleaned ITO were observed on CF_3-S, it is clearly seen that ϕ values decreased more rapidly at a high RH (ca. 90%) than those at a low RH (ca. 30–40%). The result suggests that degradation of the chemically modified ITO surfaces resulted from reaction with water. To confirm this interpretation, we also observed ϕ and CA after dipping the samples in pure water for ca. 18 h. These values are also listed in Table 1.

First, all low CA values observed on the chemically modified ITO surfaces after the dipping in pure water were almost the same as those observed on ITO(uv) after the dipping. The initial high CA values reflect SAM formation of the modifiers on the chemically modified surfaces, while the recovery of the hydrophilic surfaces by the dipping indicates clearly that almost all surface-bound modifiers were removed by the dipping. At present, the origin of slight difference in the initial CA values observed between Cl-S and Cl-P in Table 1 has not been clarified yet, but it seems likely to be due to the difference in the initial surface densities between them suggested by preliminary XPS measurements. Second, as is clear from the following logarithmic plots, ϕ values observed under the high RH were approaching the common ϕ_w of 4.7 eV observed after dipping in Table 1. But, even after one week (ca. 10000 min), ϕ observed on CF_3-S did not reach ϕ_w, while it is clear from Figure 2a that ϕ observed on ITO(uv) reached ϕ_w within a day. In other words, it is highly probable that the final states reached in air were the same as those reached in water, but the rapid degradation observed in water were greatly retarded in air even at the high RH. Third, it is likely also from the logarithmic plots that even at the low RH ϕ values were also approaching ϕ_w. But, ϕ observed on CF_3-S did not reach ϕ_w even after one month.

In the following, the rate law of the degradation process will be discussed based upon the most probable mechanism. To see more closely the decrease in ϕ as a function of the exposure time (t), we observed carefully the large change in $\phi(t)$ on CF_3-S.

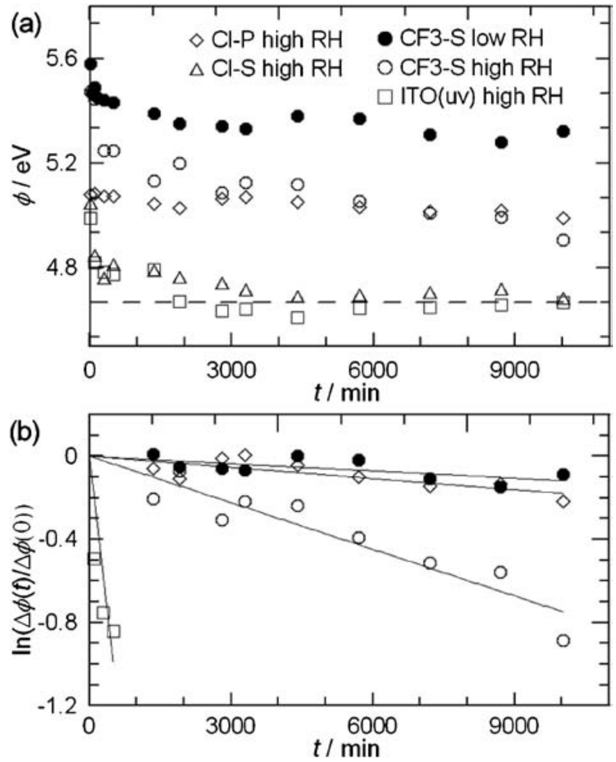

Figure 2. (a) The change in ϕ as a function of exposure time (t) for ITO(uv), CF_3-S, Cl-S, and Cl-P at high RH and CF_3-S at low RH, (b) the $\ln(\Delta\phi(t)/\Delta\phi(0))$–$t$ plots constructed from the plots in (a) except Cl-S.

Here, we assume that the degradation with water proceeds through a pseudo-first-order reaction because the presence of an excess amount of water on the surfaces is known in air.[16] We also assume that $\Delta\phi(t)/\Delta\phi(0)$ is proportional to the surface concentration of the remaining modifier,[17] where $\Delta\phi(t) = \phi(t) - \phi_w$, $\Delta\phi(0) = \phi(t = 0) - \phi_w$, and ϕ_w is the common value of 4.7 eV observed after dipping in pure water (Table 1) as described above.

In Figure 2b, values of $\ln(\Delta\phi(t)/\Delta\phi(0))$ are plotted against t for ITO(uv), CF_3-S, and Cl-P at the high RH as well as CF_3-S at the low RH. As we would expect from the assumed pseudo-first-order reaction, all plots decreased linearly with t. This observed rate law also strongly supports that water in the environments is the primary reactant in the degradation process. We also found from these plots that half-lives for ITO(uv), CF_3-S, and Cl-P at the high RH and CF_3-S at the low RH were ca. 6, 150, 640, and 980 h, respectively. It was also found that the degradation rate observed on CF_3-S was much higher than that on Cl-P.[18]

In conclusion, we studied the degradation processes and their rates of the chemically modified ITOs with acid chlorides and compared the results with those of ITO(uv) in three different environments, i.e., in water and in air with two different RHs. It was found that the chemically modified ITO surfaces were much more stable than those of ITO(uv) and that the primary reactant in the degradation was most likely to be water.

References and Notes

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12 There was no appreciable change in sheet resistance ($20\,\Omega\,\mathrm{sq}^{-1}$) after the chemical modification for 5 min with a 1 mM modifier solution in dichloromethane dehydrated. The etching with acid chlorides was retarded by the use of dehydrated solvents.
13 Because the rapid decrease in ϕ of the ITO surfaces oxidized and chemically modified afterward was observed in air within 10 h, we measured initial values of ϕ and CA within 20 min. In addition, ϕ was calibrated by comparing observed values of contact potential difference (cpd) on the modified ITO surfaces with the cpd value observed on HOPG.[14] For average cpd measurements with a Kelvin probe force microscope,[15] gold coated AFM tips chemically modified with decanethiol were used as previously.[8c]
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17 From the view point of proportionality to surface concentrations XPS was considered to be more ideal, but the $\phi(t)$ measurements were found to be preferable for kinetics from their reproducibility. For Cl-S, the kinetic analysis was difficult because of small $\Delta\phi(t)$. The much higher degradation rates observed in water than in air are partially due to slight solubility of ITO in water (see M. Pourbaix, *Atlas of Electrochemical Equilibria in Aqueous Solutions*, Pergamon Press, Oxford, **1966**).
18 This can be attributed to difference in reactivity against water between two types of surface bonds in CF_3-S and Cl-P.

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